Preparation of PVA/PAN Bicomponent Nanofiber Via Electrospinning and Selective Dissolution

Mi Nae Kim, Joonseok Koh, Yujin Lee, Hyungsup Kim

Department of Textile Engineering, Konkuk University, Seoul, Korea

ABSTRACT: Bicomponent polymer solutions were prepared from two immiscible polymers, poly(vinylalcohol) (PVA) and polyacrylonitrile (PAN), and then used to prepare films and electrospun fibers. The miscibility and the surface morphology of the bicomponent polymer systems were determined. There was a strong relationship between the diameter of the electrospun fibers and the blend ratio used. By applying selective dissolution, using solvents such as hot water, acetic acid, or N,N-dimethylformamide, to the films and fibers, one polymer component was removed selectively without affecting the other component. This resulted in a decrease in the diameter of the electrospun fibers and the formation of grooves, pores, and craters on the fiber surface. The width of the grooves decreased as the bicomponent polymer content increased. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 274–282, 2009

Key words: blends; fibers; films; immiscibility; morphology

INTRODUCTION

Arising from recent advances in nanotechnology, nanofibers can be produced using various techniques. Electrospinning is one of the simplest manufacturing techniques for making nanofibers, using various polymers, and is now considered the most feasible technology for mass production system. When high voltage is applied to polymer solutions or molten polymers, an electrical field is created between the tip and the collector. This electrical force results in the creation of nanofibers with diameters of 50–500 nm.

Most of the research carried out to date in the field of electrospinning of fibers[1–9] can be divided into three main areas: (1) maximization of the fibers' specific area by minimizing the fiber diameter using a suitable electrospinning system,[1–3] (2) manufacture of functional fibers from various polymer materials,[4,5] and (3) theoretical approaches to the electrospinning process.[6,9] The preparation of functional fibers and fine fibers from various polymeric materials has been particularly and intensively investigated.

The electrospinning of bicomponent blend solutions[3–5] is one of the most feasible methods to produce finer/functional fibers.[1–8] Spinning of a bicomponent blend can simultaneously yield finer fibers and functional fibers if an appropriate polymer pair is selected. The miscibility of the two polymers is an important parameter in bicomponent blend spinning. Several researchers have reported on the phase morphology and the miscibility of blend systems or copolymers.[7,8,10,11] Youk and coworkers[4,5] produced porous ultrafine fibers from immiscible polymers after inducing phase-separated morphology via electrospinning.

To understand the spinability and electrospun fiber morphologies from bicomponent polymer solutions, poly(vinylalcohol) (PVA) and polyacrylonitrile (PAN) bicomponent solutions were produced with various blend ratios for electrospinning. These polymers were selected to simultaneously reduce the fiber diameter and improve the spinnability. Although PVA can produce fibers with diameters of less than 200 nm, using electrospinning, it shows poor spinnability and bead formation. PAN shows good spinnability and produces nanofibers with fiber diameters of less than 500 nm.[12] The cast films and electrospun webs produced from PVA/PAN bicomponent polymer solutions were treated with hot water or acetic acid to remove the PVA selectively. The PAN was removed by N,N-dimethylformamide (DMF) treatment. The morphological and the physical changes caused by these treatments were studied. After treatment, the electrospun web showed various irregularities on the fiber surface, such as grooves, pores, and craters, which resulted in the web having a higher specific area when compared with the nontreated web.

TABLE I
Concentration of PVA/PAN Bicomponent Polymer Solutions

Condition	Levels
Total concentration (wt %)	15, 17, 19
Content (PVA/PAN) (w/w %)	100/0, 75/25, 50/50, 25/75, 0/100

EXPERIMENTAL

Materials

PVA (M_w 70,000–100,000, hot water soluble, Sigma) and PAN (M_w 80,000–100,000) were dissolved in dimethyl sulfoxide (DMSO, 99.9+%, Burdick and Jackson), in various blend ratios (15–19 wt %), as given in Table I. Each of the solutions was used for film casting and for electrospinning.

Sample preparations

PVA/PAN bicomponent films and fibers were prepared using the solutions given in Table I. To observe the miscibility between the two polymers, films were cast on glass slides and then dried in a vacuum oven at 60°C. PVA/PAN solutions were electrospun with a syringe system and collected on aluminum foil. The processing conditions used for electrospinning are given in Table II.

Selective dissolution

PVA (here, the target polymer for elimination) is a water-soluble polymer, and PAN is insoluble in water. PVA was successfully removed from the cast films, and electrospun webs were prepared from the bicomponent polymer mixtures by immersing them in hot water (80°C) for 1 h, followed by drying in a convection oven for 30 min at 60°C. PVA can also be removed using acetic acid. PAN was removed from the bicomponent polymer using DMF in the similar way.

Morphological properties

Changes in the surface of the cast bicomponent films after the hot water treatment were determined using an optical microscope (SV 32, iCamscope, Sometech, Korea) and scanning electron microscope (SEM, JSM 6380, JEOL, Japan). Changes in the morphology of the electrospun fibers after the hot water treatment were observed using SEM, and the fiber diameter distribution was determined from the SEM images, using an image process developed in our research group and an EyeView analyzer image program.

Polymer identification

Changes in the compositions of the cast films and the electrospun webs after the hot water treatment were observed using a Fourier transform infrared spectrometer (FTIR– 300E, Jasco, Japan).

Thermal properties

The thermal properties of the electrospun PVA/PAN webs were determined using a differential scanning calorimeter (DSC 2010, TA Instruments). The transition temperature and the heat of fusion were measured for each bicomponent polymeric mixture, both before and after the hot water treatment.

RESULTS AND DISCUSSION

Composition of PVA/PAN bicomponent films

Figure 1 shows the surfaces of the PVA/PAN bicomponent films as observed by optical microscopy.

The bicomponent films were composed of two separate phases: a continuous phase and a disperse phase. The polymer constituting the continuous phase generally changed according to the relative amount of the polymer. The polymer with the higher content constituted the continuous phase, whereas the other polymer constituted the dispersed phase. The shape and the size of the dispersed domain also changed with the blend ratio. Optical microscopy also confirmed that PVA was successfully and selectively removed from the bicomponent film by immersion in hot water for 1 h. When the PVA content (%) in the film was lower, the PVA was more easily removed. In the case of the 25/75 (PVA/PAN) film, the PVA was easily removed by hot water; it could be observed with the naked eye.

Changes in the microscopic morphology after hot water treatment were determined by recording SEM images of the films (Fig. 2). The pictures in the left-hand column (a, c, and e) are the SEM images of the films prepared from bicomponent polymer solutions of various blending ratios before the hot water treatment, and the ones in the right-hand column (b, d, and f) are the SEM images after the treatment.

TABLE II
Electrospinning Conditions of PVA/PAN Bicomponent Polymers

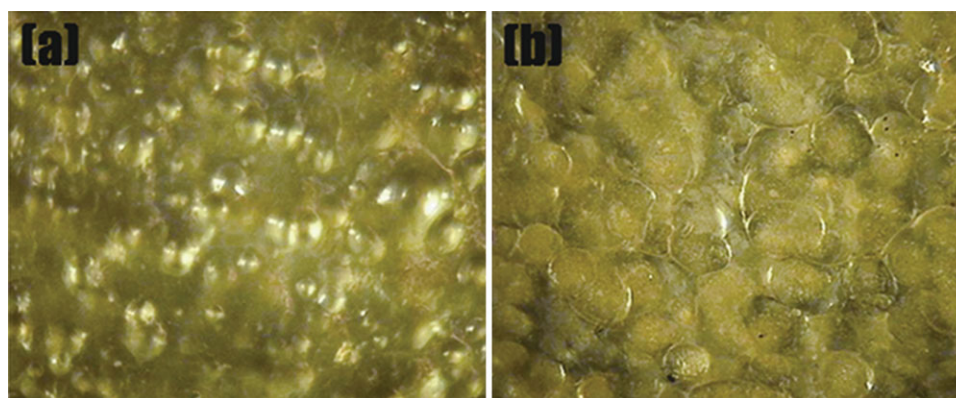| Condition	Levels
TCD (cm)	15
Applied pressure (kPa)	69
Applied voltage (kV)	18, 21, 24, 27, 30

Figure 1 Microscopic images of 75/25 film with the magnification ratio of 300: (a) before and (b) after treatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
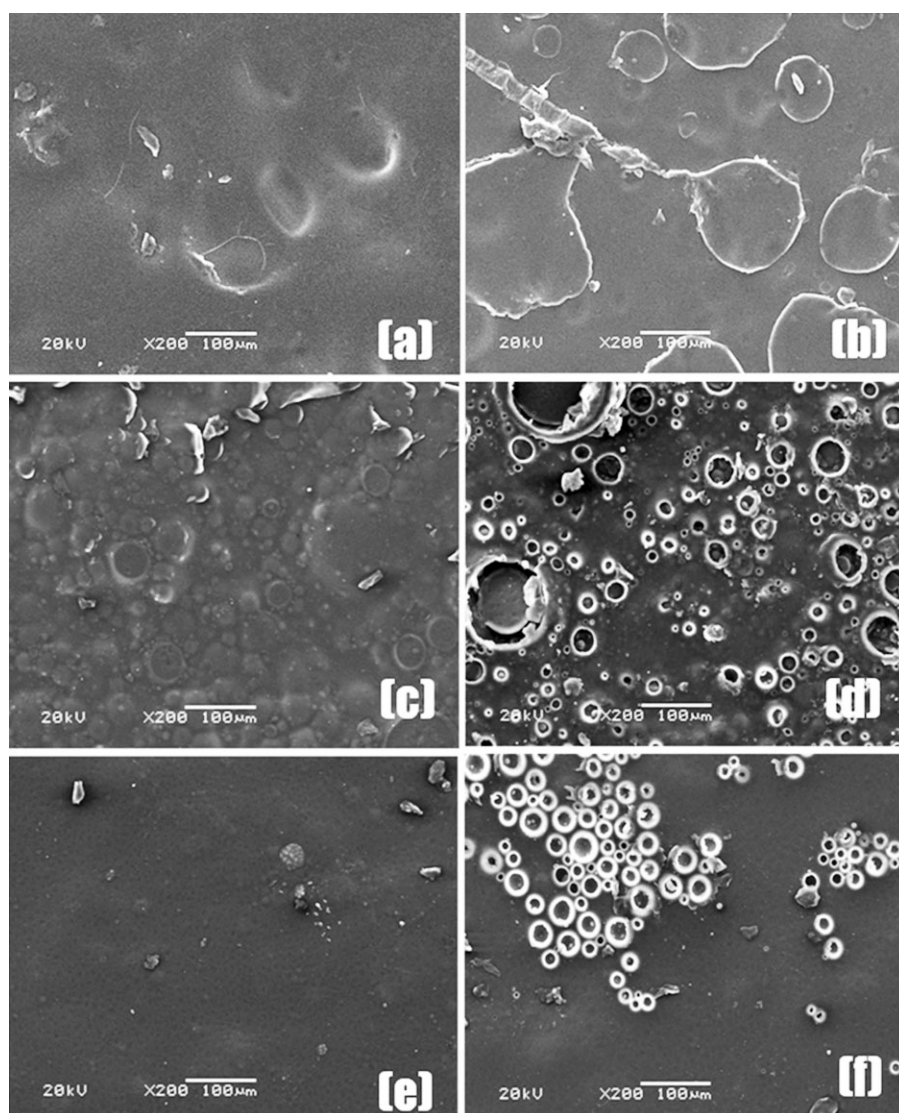

Figure 2 SEM images of bicomponent polymer films: (a) before the hot water treatment for PVA/PAN = 75/25; (b) after the hot water treatment for PVA/PAN = 75/25; (c) before the hot water treatment for PVA/PAN = 50/50; (d) after the hot water treatment for PVA/PAN = 50/50; (e) before the hot water treatment for PVA/PAN = 25/75; and (f) after the hot water treatment for PVA/PAN = 25/75.

Although the boundary between the PVA and the PAN was not clearly observed before the treatment, it became clearer after removal of the PVA. When the PVA content was 75% (and PAN 25%), the continuous phase comprised PVA and the granule-shaped disperse phase comprised PAN. After the hot water treatment, several large granules remained, as illustrated in Figure 2(b). The granules comprised PAN, as determined by IR spectroscopy (see Fig. 3), and their average diameter was about 36 μm.

When the PAN ratio was increased to over 50%, the continuous phase changed from the PVA to the PAN. The treatment resulted in pores and craters on the surface of the film because of the PVA removal. The average crater size and the total crater volume decreased as the PAN content increased, as shown in Figure 2(d,f). More of the larger craters were observed in the case of 50/50 than 25/75 (PVA/PAN). The average sizes of the craters were about 25 and 12 μm, respectively. This suggests that the dispersibility improved as the ratio of the PAN component increased.

FTIR analysis also confirmed the successful removal of the PVA by hot water treatment. The PVA has a characteristic peak at 3400–3300 cm^{-1}, ascribed to the —OH groups, and the PAN has a characteristic peak at 2250 cm^{-1}, ascribed to the —CN groups. Figure 3 shows the IR spectra of PVA/PAN films prepared from a 17 wt % bicomponent polymer solution, with a blend ratio 50/50, before and after the hot water treatment. The IR spectrum of the non-treated film showed characteristic peaks of both PAN (—CN peak at 2250 cm^{-1}) and PVA (—OH peak at 3400–3300 cm^{-1}). However, after treatment, the peak at 3400–3300 cm^{-1} became smaller and then disappeared, whereas the peak at 2250 cm^{-1} became larger. The results of samples prepared from bicomponent solutions of other ratios showed similar results. This indicated that the PVA was successfully removed from the film by this treatment. Some samples did, however, still show indications of the characteristic peak of the —OH group, albeit in decreased size, which meant that some PVA still remained, and hence further treatment was required to remove the PVA completely.
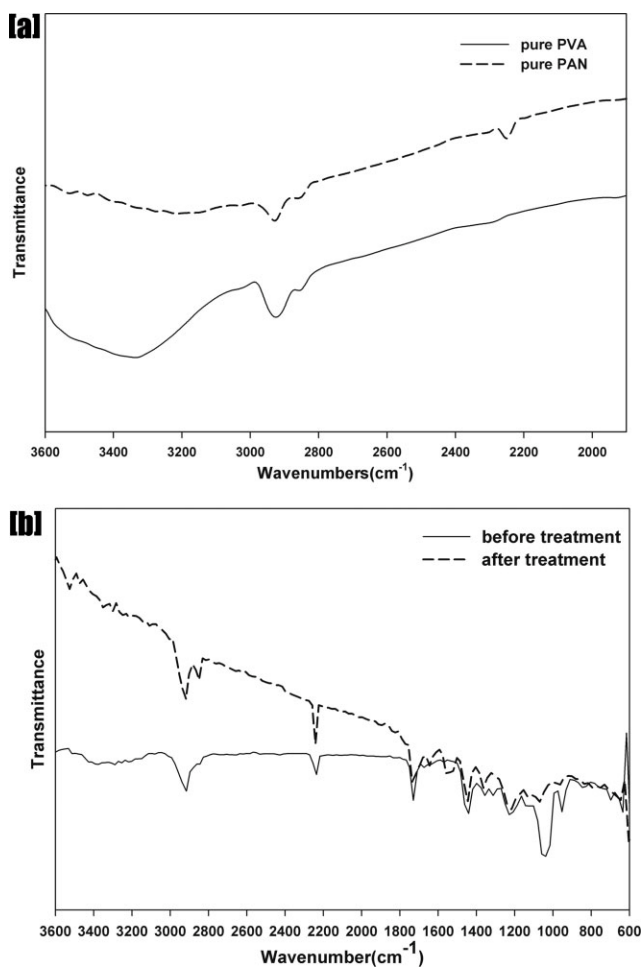
Electrospinning of PVA/PAN bicomponent polymers

The PVA/PAN bicomponent polymers and the PVA and PAN homopolymers were electrospun under various processing conditions (see Table II). Figure 4 shows SEM images of the PVA/PAN electrospun webs of various blend ratios, prepared under the same electrospinning conditions. The homo PVA [Fig. 4(a)] showed poor spinnability when compared with the homo PAN [Fig. 4(e)], irrespective of the total solution concentration used. Solution droplets were often observed during the electrospinning of homo PVA, and the resultant fibers had many defects. The blended polymer solutions showed spinnability between that of the homo PVA and the homo PAN solutions. The spinnability of the blended solution was improved when the ratio of the PVA content was increased, and defects such as beads and droplets in the web were reduced.

Figure 5 shows the average fiber diameter in the webs as a function of the PVA/PAN ratio for various total solution concentrations. There was a significant relationship between the average fiber diameter and the PVA/PAN ratio when the total concentrations were 17 and 19 wt %. As the PAN ratio increased, so did the average fiber diameter, up to a certain level. A further increase in the PAN content ratio resulted in a smaller average diameter. This can be explained in terms of the dipole interaction between the side groups of the two polymers. Both the hydroxyl group (—OH) and the cyanonitrile group (—CN) have partial negative dipoles. As a

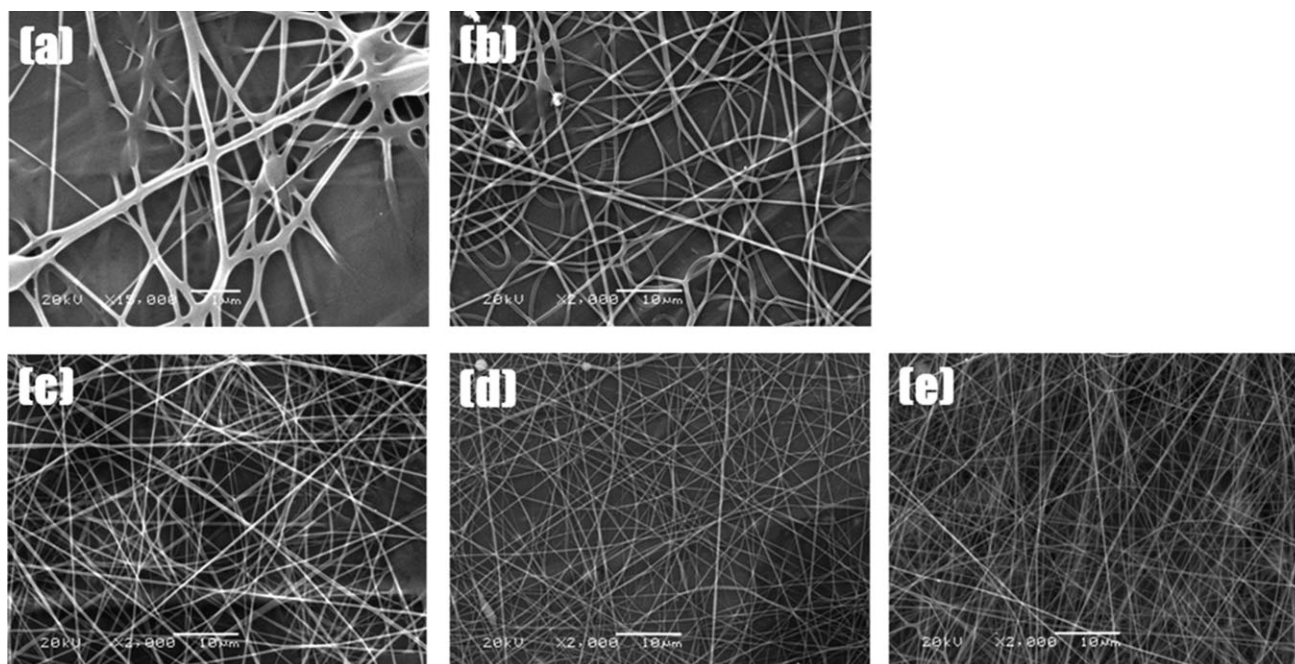**Figure 3** FTIR spectra of (a) pure PVA and PAN and (b) 50/50 PVA/PAN films.

Figure 4 SEM images of PVA/PAN nanofibers produced under the same electrospinning conditions: (a) PVA, (b) 75/25, (c) 50/50, (d) 25/75, and (e) PAN.

result, the repulsive force between the two polymers induces volumetric inflation. There was, however, no significant relationship between the average fiber diameter and the blend ratio when the total solution concentration was 15 wt %. The spinning behavior of the 15 wt % solution was not stable, and some parts of the resulting fibers were neither fully extended by whipping nor fibrillated by splaying.

Morphology of PVA/PAN electrospun webs after hot water treatment

Figure 6 shows the SEM images of the bicomponent fiber webs electrospun from a 17 wt % solution. The SEM images in the left-hand side column (a, c, and e) illustrate the bicomponent fiber webs before the treatment, and the images in the right-hand side column (b, d, and f) after the treatment. The bicomponent fibers had a smooth surface before the hot water treatment.

However, as the PVA was removed by the treatment, the average fiber diameter decreased and the surface became rough. The change in the surface morphology and the decrease in fiber diameter reduction were dependent on the blend ratio. When the PVA constituted the continuous phase, the hot water treatment resulted in irregularities.

The following is a possible explanation for this. The large separated PAN granule-type domains were linked to each other as the continuous phase (PVA) was removed. When the PAN was the continuous phase, the separated PVA domains on the fiber

surface were removed, as shown in Figure 6(d,f). Removal of the PVA resulted in the creation of long grooves along the fiber axis on the surface. This arose from fiber elongation by the whipping motion during electrospinning. The PVA phase was also subjected to tensile force created by the electrical force and the instability. The average groove width was 20–40 nm, which decreased as the PAN content increased. This result was not coincident with that of other researchers.[4,5] In other earlier studies, the selective removal created round-shaped craters and porous fibers were obtained. These craters and pores may be caused by different solidification times. If the solidification time is long enough, then the
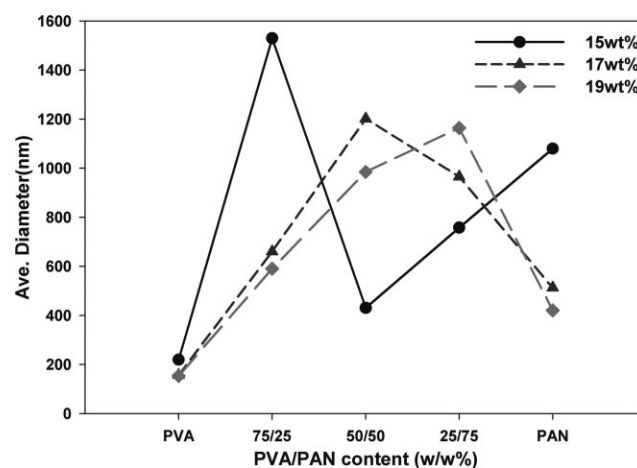

Figure 5 Average fiber diameter change of PVA/PAN nanofibers along bicomponent ratios.
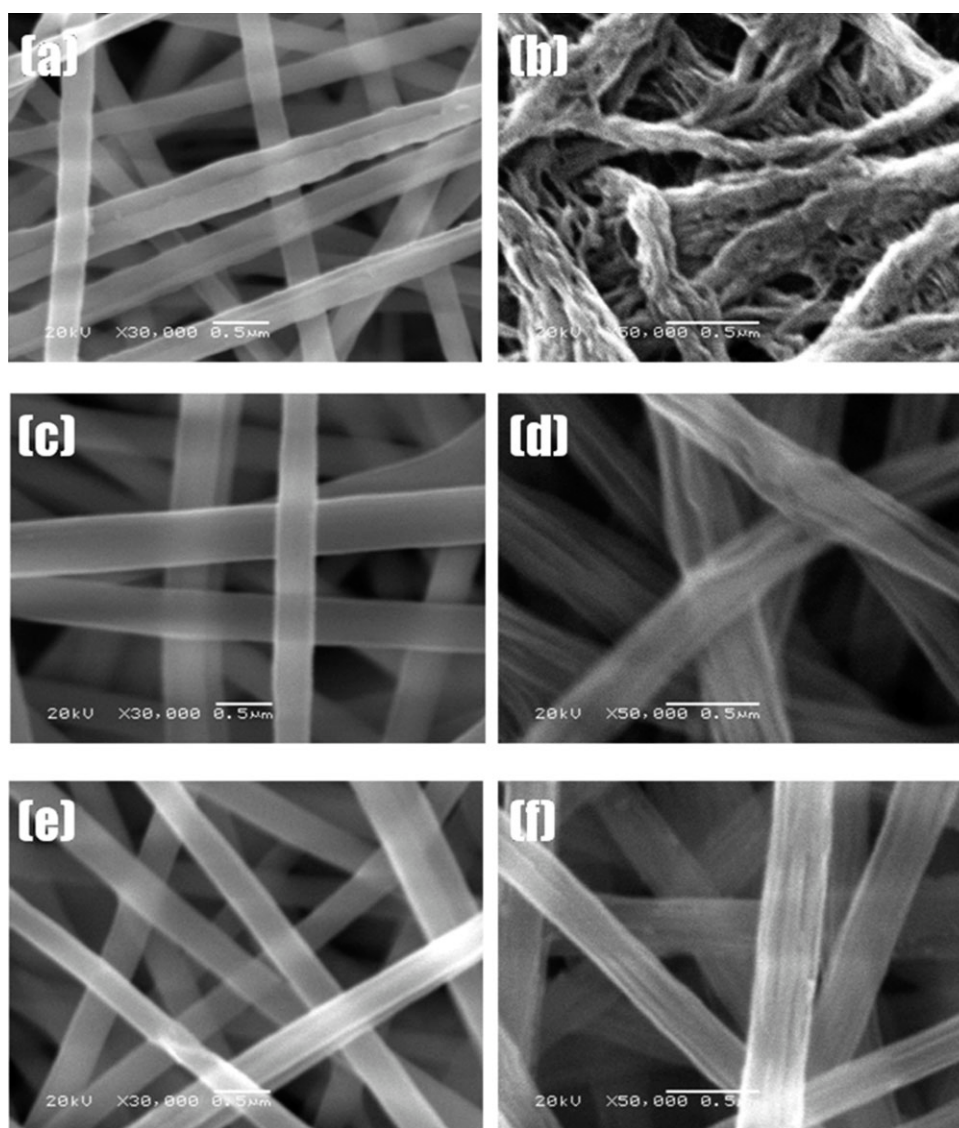
Figure 6 SEM images of electrospun webs at the total concentration of 17 wt %: (a) before the hot water treatment for PVA/PAN = 75/25; (b) after the hot water treatment for PVA/PAN = 75/25; (c) before the hot water treatment for PVA/PAN = 50/50; (d) after the hot water treatment for PVA/PAN = 50/50; (e) before the hot water treatment for PVA/PAN = 25/75; and (f) after the hot water treatment for PVA/PAN = 25/75.

separated domain assumes a spherical shape, as a result of surface tension, after fiber formation. However, if the solidification time is relatively short, then the elongated shape remains.

As shown in Figure 7, the average fiber diameter also decreased after the treatment. The extent of the decrease in the average fiber diameter in the case of the 50/50 PVA/PAN web was greater than the other blend ratios. Despite the 75/25 PVA/PAN bicomponent polymer having the higher PVA content, the decrease in its fiber diameter after treatment was smaller than the 50/50 blend ratio. This was due to the readhesion of the dissolved PVA; some PVA was not washed out during the hot water treatment and it adhered to the fiber surface. The average fiber diameters of the treated 75/25 PVA/PAN webs

were similar to the diameters of the untreated homo PVA fibers. Similarly, the diameters of the 25/75 PVA/PAN fibers were decreased by the hot water treatment.

Composition of PVA/PAN electrospun webs

FTIR was used to verify changes in composition of an electrospun web after the hot water treatment. IR spectra of an electrospun web (19 wt %, 75/25 PVA/PAN) before and after treatment are shown in Figure 8. Characteristic peaks are seen at 3400–3300 cm^{-1} (—OH) and 2250 cm^{-1} (—CN). After the treatment, the —OH peak became smaller and the —CN peak became larger. Similar to the results obtained for the films, the —OH peak was still to be
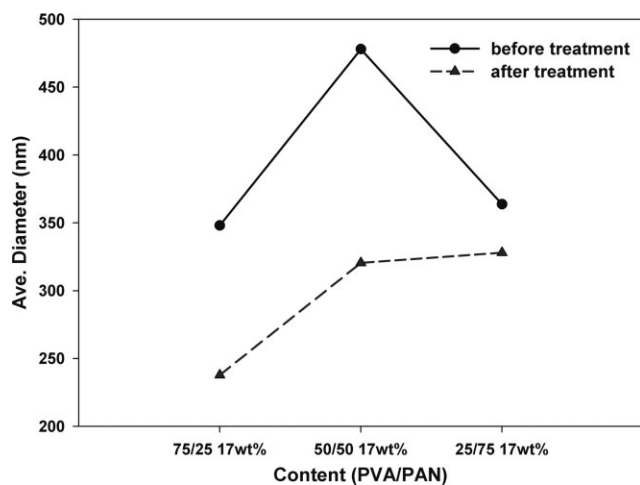
Figure 7 Average fiber diameter of PVA/PAN webs spun from a 17 wt % bicomponent polymer solution before and after hot water treatment.

seen in some samples because of the incomplete PVA removal.

Thermal properties of PVA/PAN electrospun webs

The homo PVA used in this study showed a melting temperature around 220°C, and the homo PAN thermally decomposed above 250°C. Figure 9 shows the DSC thermograms of electrospun webs of PVA/PAN (17 wt %, 75/25) before and after treatment. Table III summarizes the transition temperatures and the heats of fusion at the transition peaks.

The PVA/PAN electrospun webs had a transition temperature around 220°C and the thermal decomposition. The webs retained the thermal characteristics of the PVA and the PAN after the treatment. However, the heat of fusion of the transition peak
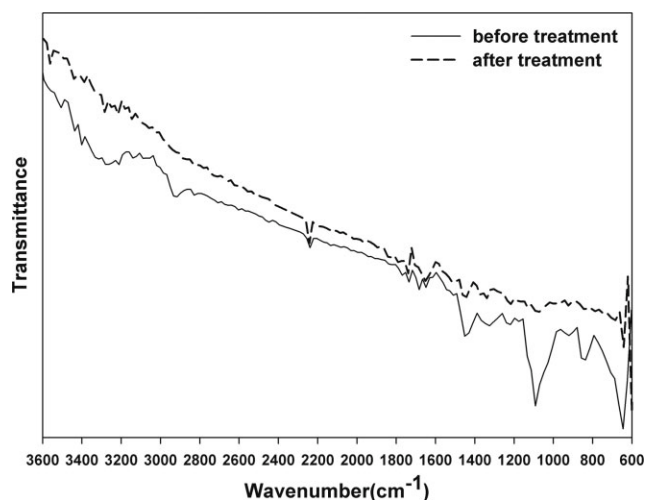

Figure 8 IR spectra of 75/25 PVA/PAN electrospun web produced from a 19 wt % bicomponent polymer solution.
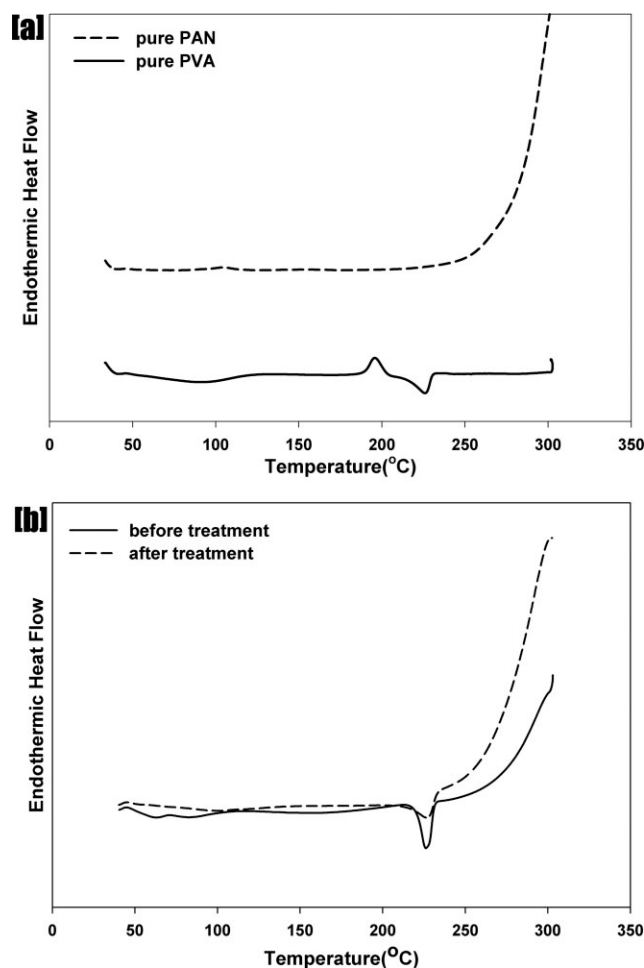
Figure 9 DSC thermograms of electrospun web produced from 17 wt % bicomponent polymer solutions: (a) pure PVA and PAN and (b) 75/25 (PVA/PAN).

decreased, confirming the removal of the PVA. The PVA transition peak could be caused by the readhesion of the PVA. The transition temperature (around 220°C) increased after the hot water treatment. It was suggested that the thermal properties were more affected by the PAN component, as the PVA was removed by this treatment. When the PAN/PAN ratio was 25/75, the increase was higher (by about 5°C) than in the case of the other ratios and it increased further as the PAN content increased. As

TABLE III
Thermal Properties of PVA/PAN Electrospun Web

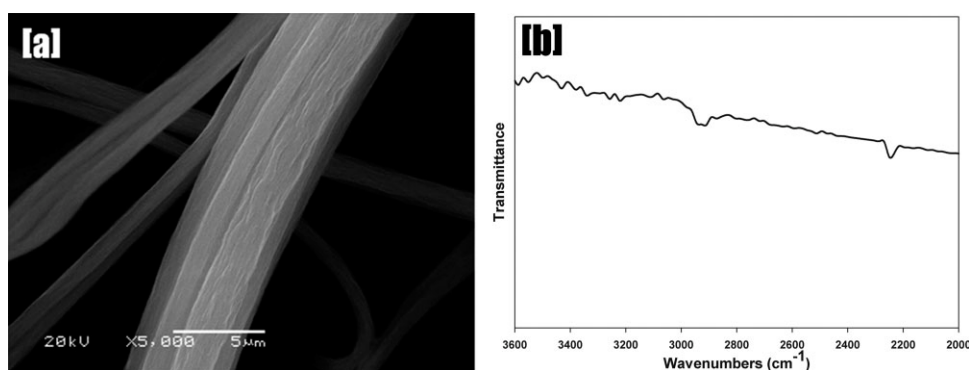| Sample (PVA/PAN)	Hot water treatment	Transition temp. (°C)	ΔH_T (J/g)
75/25	Before	226.14	19.17
17 wt %	After	227.15	14.90
50/50	Before	227.40	22.63
17 wt %	After	229.39	7.39
25/75	Before	220.59	11.53
17 wt %	After	225.44	10.06

Figure 10 Nanofiber prepared from a 17 wt % bicomponent solution, blend ratio 25/75 PVA/PAN, after acetic acid treatment: (a) SEM image and (b) FTIR spectrum.

the PVA content decreased, the hot water treatment removed the PVA more effectively. The heat of fusion decreased after the treatment. These changes resulted from the removal of the PVA.

The effect of acetic acid treatment

In an alternative dissolution method, acetic acid was used to remove the PVA. Figure 10 shows the SEM image and the FTIR spectrum of a bicomponent PVA/PAN (25/75) nanofiber after the acetic acid treatment. The fibers had irregular surfaces and long grooves, similar to fibers after hot water treatment. The PVA was successfully removed from the fibers prepared from a bicomponent polymer solution with a blend ratio of 25/75 while the other fibers still contained PVA because of the inadequate treatment. As similar to the result of the hot water treatment (Fig. 3), FTIR also indicates that PVA was removed successively by the treatment.

The effect of DMF treatment

DMF was used to remove the PAN from the PVA/PAN nanofibers. Because PVA also dissolves in

DMF at high temperature, the PVA/PAN electrospun webs were treated with DMF at room temperature for several minutes. Figure 11 shows the SEM image and the FTIR spectrum of bicomponent PVA/PAN (50/50) nanofiber after the DMF treatment. The fiber surface became rough and grooves could be seen, as was the case after the other treatments. However, instead of the disappearance of characteristic —OH peak, the —CN peak (2250 cm^{-1}) decreased.

Proposed morphological model

Arising from these results, we suggest a morphological model to explain the PVA/PAN bicomponent fiber formation (see Fig. 12). The separated and the dispersed phases are determined by the volume fraction and the miscibility or the dispersibility of the two polymers. During electrospinning, the repulsive forces of the hydroxyl group (—OH) and the cyanonitrile group (—CN) increase as a result of the electrical charge because of having the same partial negative dipole. During electrospinning, the electrical force results in elongational stress as well as instability of the jet. During the whipping motion,
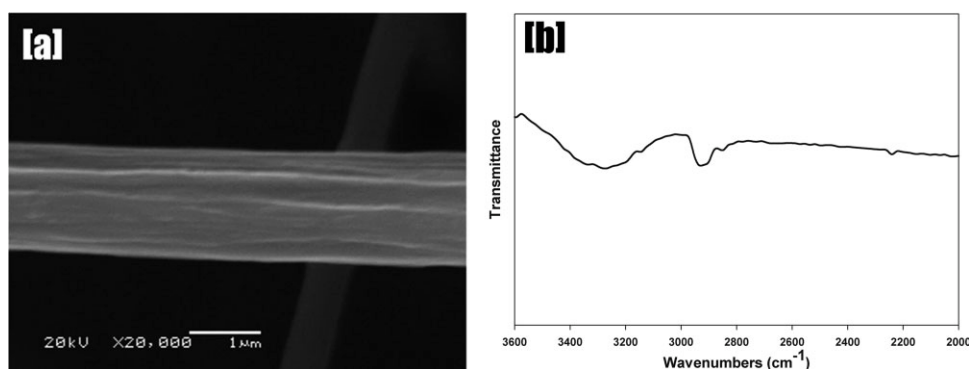

Figure 11 Nanofiber prepared from a 17 wt % bicomponent solution, blend ratio 50/50 PVA/PAN, after DMF treatment: (a) SEM image and (b) FTIR spectrum.
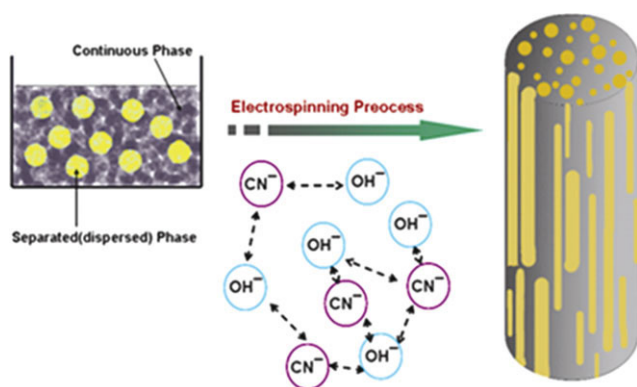
Figure 12 Schematic representation of the electrospun fiber from PVA/PAN bicomponent solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the fiber is drawn and the dispersed domains cannot sustain the spherical shape and is elongated as the jet. As a result, the fiber has the sea–island type morphology.

CONCLUSION

PVA/PAN bicomponent fibers were successfully prepared using electrospinning. The immiscibility of the two polymers was confirmed both in the films and in the electrospun fibers by FTIR. The PVA/PAN had better spinnability than the homo PVA solution. When the spinning behavior was stable, the fiber diameter increased with the PAN content ratio

because of the repulsive forces acting between the side groups of the two polymers. To remove the PVA selectively, the fibers were immersed in hot water or acetic acid. Most of the PVA was removed by these treatments. Treatment resulted in a decrease in the diameter of the electrospun fibers and the appearance of grooves on the fiber surfaces along the fiber axis. The width of the groove decreased as the PAN content increased. PAN was successfully removed by DMF treatment, and the resulting surface had grooves similar to those observed after PVA removal.

References

1. Dinga, B.; Kimura, E.; Sato, T.; Fujita, S.; Shiratoria, S. Polymer 2004, 45, 1895.
2. Zhao, Q.; Huang, Z.; Wang, C.; Zhao, Q.; Sun, H.; Wang, D. Mater Lett 2007, 61, 2159.
3. Gupta, P.; Wilkes, G. L. Polymer 2003, 44, 6353.
4. You, Y.; Youk, J. H.; Lee, S. W.; Min, B. M.; Lee, S. J.; Park, W. H. Mater Lett 2006, 60, 757.
5. Han, S. O.; Son, W. K.; Hoc, D.; Youk, J. H.; Park, W. H. Polym Degrad Stab 2004, 86, 257.
6. Babel, A.; Li, D.; Xia, Y.; Jenekhe, S. A. Macromolecules 2005, 38, 4705.
7. Lednický, F.; Hromádková, J.; Kolařík, J. Polym Test 1999, 18, 123.
8. Salmoria, G. V.; Leite, J. L.; Ahrens, C. H.; Lago, A.; Pires, A. T. N. Polym Test 2007, 26, 361.
9. Oh, J. S.; Jang, J. G.; Bae, Y. C. Polymer 1997, 38, 3761.
10. Aouachria, K.; Belhaneche-Bensemra, N. Polym Test 2006, 25, 1101.
11. Chiu, F.; Ting, M. Polym Test 2007, 26, 338.
12. Ryu, G. S. MSc Thesis, Konkuk University, Korea, 2006.